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Article

Enhancement of Stability in Alkali Solution of Polyethylene Terephthalate Fibers using Low-Dose Gamma Irradiation for Fiber-Reinforced Neutron Shielding Concrete

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Abstract. Polyethylene terephthalate (PETE) fibers are used as a reinforcing agent to enhance concrete strength as well as to shield against thermal neutrons. This study increased the stability of PETE fibers in a strong alkali solution characteristic of concrete (pH = 12) using low-dose gamma radiation to induce crosslinking of the polymer chains. Results indicated that gamma ray dose of only 30 kGy resulted in the highest molecular weight, tensile strength and degree of crystallinity of PETE fibers with size 1.3 D. The surface topology using SEM micrography were also evaluated. An accelerated age testing revealed that these radiation-treated fibers will maintain their mechanical strength in concrete for up to at least 60 months. Thermal neutron attenuation test of fiber-reinforced concrete (FRC) indicated that the degree of thermal neutron shielding increased with increasing PETE fiber content, and that at 0.3% fiber content, FRC exhibited the highest thermal neutron attenuation of about 60% compared to unreinforced concrete. Therefore, these FRCs can readily be utilized as an effective neutron shielding material for nuclear and radiation applications to enhance radiation safety.

Keywords: Gamma ray, molecular weight, polyethylene terephthalate fiber, alkali solution, fiber reinforced concrete, neutron attenuation.

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1. Introduction

Polyethylene terephthalate (PETE) is a polymer that is widely used in several forms such as fibers, films or even containers such as drinking water bottles. This is because the polymer exhibits many advantageous properties such as dielectricity, resistance to several organic acids, resistance to water, resistance to tensile stress up to around 172 MPa, which is 2 - 3 times higher than that of cellophane and cellulose acetate, and reasonable toughness [1]. Because of its excellent mechanical properties, demands for PETE are high, resulting in generation of large amount of waste. Moreover, used products containing the polymers have been widely recycled.

A high molecular weight of a polymer usually results in enhanced mechanical properties such as high strength, high toughness and high density [2-3]. The present research attempted to increase the molecular weight of PETE using gamma irradiation because the ionizing radiation can result in crosslinking of several polymer chains, creating a 3-dimensional structure and enhancing mechanical properties [4]. The relationship between gamma dose and molecular weight of the polymer was studied. Previously, there have been several studies on the effect of gamma radiation on the strength of the polymer. Jeon et al. reported that Young's modulus and elongation at break of PETE increased with increasing gamma irradiation dose in the range 0 - 200 kGy [5]. Buttafava et al. reported that the melting heat of the polymer increased with increasing gamma ray dose [6]. However, these studies employed a relatively high gamma irradiation dose. A study on low-dose irradiation has not been performed.

PETE is one among several polymers widely used in civil engineering because it can be fabricated into fibers to reinforce concrete [7] to enhance mechanical properties [8]. In addition, fiber reinforced concrete (FRC) exhibits excellent neutron attenuation, allowing it to be utilized as an effective neutron shielding material for nuclear and radiation applications. When the fibers were added to concrete, mechanical properties varied with fiber contents [9-11], but the strength of concrete always increased. This demonstrates the practical applications of the PETE fibers with concrete to strengthen the material [12-13]. When PETE fibers are added into concrete, the fibers are subjected to a strong basic condition (pH $\approx$ 12) because concrete naturally exhibits high alkalinity. The polymer normally cannot withstand a basic condition and will degrade [14-15]. This is the limitation of using PETE fibers to reinforce concrete. Some researchers suggest that the molecular weight of PETE fibers becomes lowered with degradation [16-20]. Thus, the present work focuses on utilizing low-doses gamma irradiation (0 – 100 kGy) to modify the molecular weight of the polymer in an attempt to improve its durability in an alkali solution. The present research compared the stability in a strong alkaline solution (pH = 12) of unirradiated and irradiated PETE fibers of various diameters under accelerated age testing. The molecular weight of specimens was measured to determine its strength after several durations of accelerated age testing. Finally, a neutron attenuation test was performed to determine the thermal neutron shielding efficiency of FRC with various radiation-treated PETE fiber contents and sizes.

2. Materials and Methods

2.1. Materials

PETE fibers were obtained from Ang-Tai Company in Thailand. Table 1 shows the measured properties of the fibers.

Table 1. Characterization of PETE fibers used in the present study.

Property	Value
Density [a]	1.37 g/cc
Glass transition temperature [b]	67 ^{o}C
Melting temperature [b]	254.3 ^{o}C
Degree of crystallinity [c]	39.68
Number average molecular weight [d]	22,455 $\pm$ 196 g/mol

[a] Measurement performed at 25 ^{o}C; [b] Performed using differential scanning calorimeter (Netzsch, DSC204F1) with temperature increment rate of 10 ^{o}C/min and temperature range of -100 – 300 ^{o}C; [c] Performed using XRD (Bruker, D8 Advance); [d] Measured using membrane osmometry method discussed in Section 2.3.

NaOH of analytical grade was purchased from Chemipan Company and was used as received without any further purification.

2.2. Gamma Irradiation

PETE fibers were irradiated with gamma radiation using Gamma cell (Gamma 220 Excel) at Thailand Institute of Nuclear Technology (Public Organization). The absorbed dose rate was approximately 5 kGy/hr and the irradiation chamber temperature was about 40 ^{o}C. Irradiation was performed in an open-atmosphere condition.

2.3. Molecular Weight Measurement Following Accelerated Age Testing

The molecular weight of PETE specimens was measured after specimens underwent the accelerated age testing at 70 ^{o}C in a strong NaOH basic solution (pH = 12). A membrane osmometry method was utilized. A 1 % (mass/vol) solution of PETE was prepared using DMSO as a solvent at 95 ^{o}C and 1 atm. Then, the calculus processes were used to reduce the Van't Hoff equation, which eventually led to the determination of the molecular weight of the fibers [10]. Figure 1 shows the apparatus setup of the membrane osmometry method.

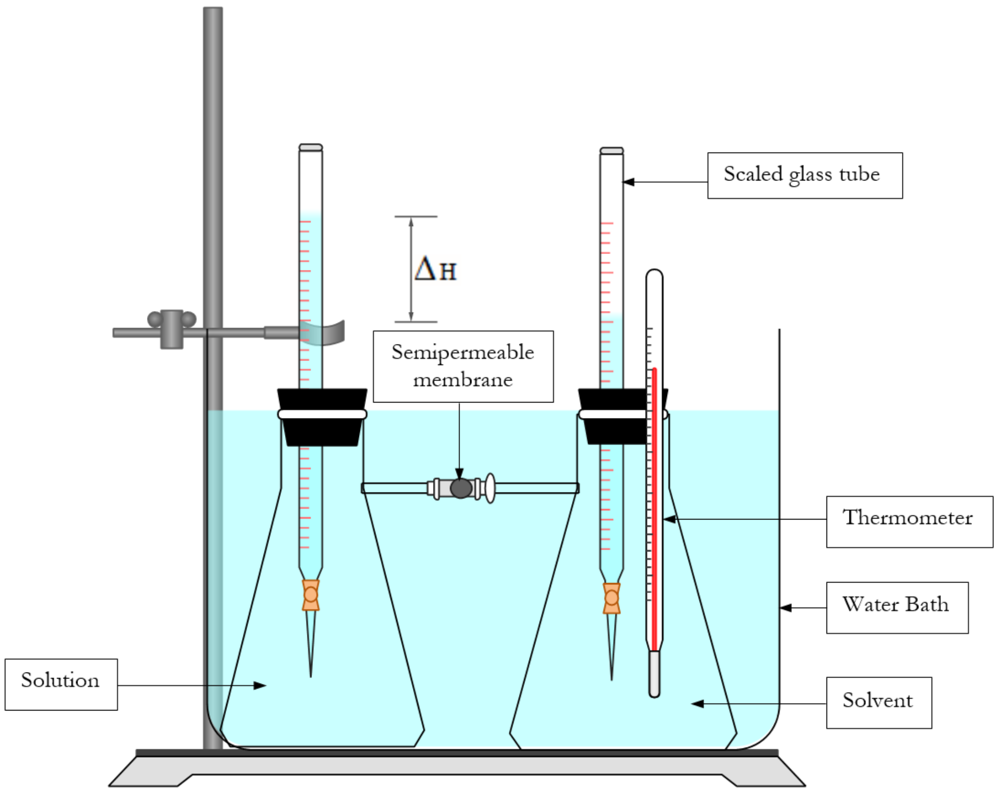

Fig. 1. Setup of membrane osmometry method.

2.4. Concrete Casting and Thermal Neutron Attenuation Test

The concrete mix composed of ordinary Portland cement, water, sand, coarse aggregate, admixture (polycarboxylate ether-based superplasticizers; PCEs) and fibers. Table 2 presents mix proportion of the concrete. In Table 2, OPC denotes concrete without fiber reinforcement; FRC-1.3D-x denotes concrete with x% of 1.3 D fibers, and FRC-25D-x denotes concrete with x% of 25 D fibers. For both fiber sizes, the PETE fiber volume fractions were 0.1, 0.2 and 0.3 % of concrete volume. The concrete was cast into cubic samples (100 x 100 x 100 mm). After 28 days of curing under water, the concrete specimens were taken out of water and were left for one day before undergoing the neutron attenuation test.

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Table 2. Mix proportion of concrete.

Designation	Cement (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	Coarse aggregate (kg/m^3)	Admixture (kg/m^3)	Fiber size	Fiber content (%)
OPC	465	200	697	999	2.33	-	0
FRC-1.3D-0.1	465	200	697	999	4.65	1.3 D	0.1
FRC-1.3D-0.2	465	200	697	999	4.65	1.3 D	0.2
FRC-1.3D-0.3	465	200	697	999	4.65	1.3 D	0.3
FRC-25D-0.1	465	200	697	999	4.65	25 D	0.1
FRC-25D-0.2	465	200	697	999	4.65	25 D	0.2
FRC-25D-0.3	465	200	697	999	4.65	25 D	0.3

The neutron attenuation test was performed by placing the concrete sample on a platform. Fast neutrons from a neutron source underwent moderation by collision with paraffin plates to become thermal neutrons before entering the sample. A ^{241}Am-Be neutron source with the dose rate of 29.08 mR/h was utilized. A BF_3 proportional tube was used to detect thermal neutrons passing through the sample. Figure 2 illustrates the schematic diagram of the neutron attenuation test. Neutron attenuation can be calculated according to the following equation:

$$\mathrm{NAT}(\%) = \frac{\mathrm{I}-\mathrm{P}}{\mathrm{I}} \times 100\,, \tag{1}$$

where NAT = Thermal neutron attenuation percentage (%)
I = Thermal neutrons impinging on specimen
P = Thermal neutrons passing through specimen.

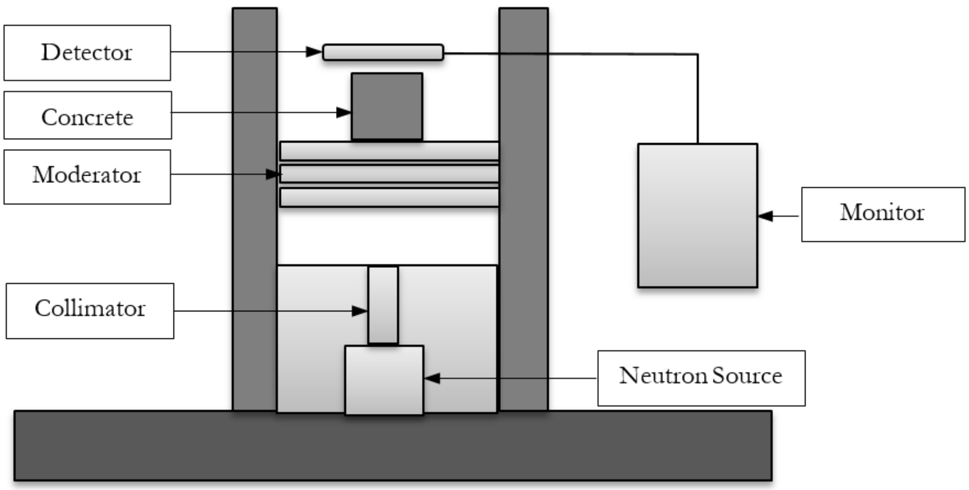


Fig. 2. Schematic diagram of neutron attenuation test.

3. Results and Discussion

3.1. Molecular Weight Reduction with Gamma Irradiation

Figure 3 demonstrates the molecular weight of PETE fibers following gamma ray irradiation. Molecular weight measurement was performed three times and the reported values represent the average ones.

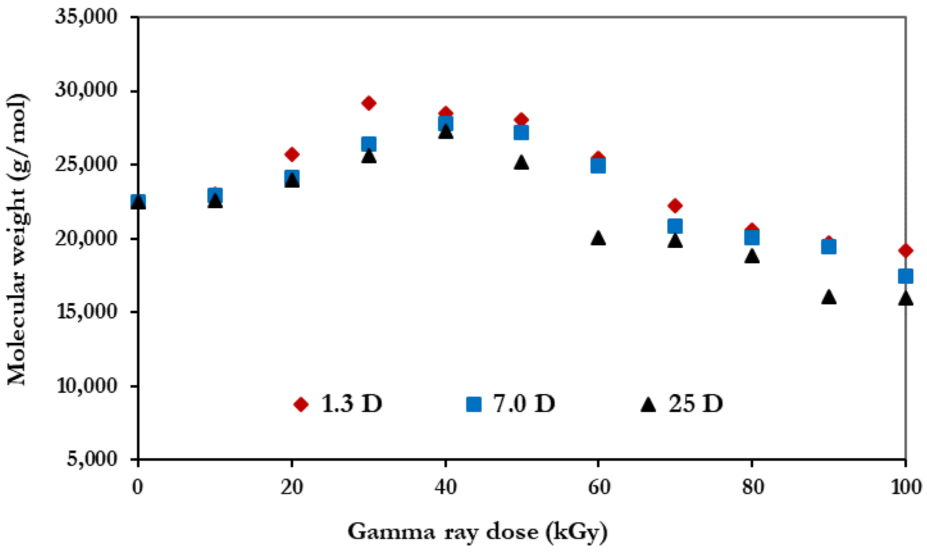


Fig. 3. Molecular weight of PETE fibers following gamma ray irradiation.

From Fig. 3, PETE fibers of size 1.3 D, the smallest size used in the experiment, and the gamma dose of 30 kGy offered the highest molecular weight. For the other two fiber sizes (7 D and 25 D), gamma ray dose of 40 kGy was the optimized one. The smallest fiber size exhibited the highest molecular weight increase following gamma irradiation. Finally, crosslinking was the dominant mechanism up to the dose of around 30 – 50 kGy. For gamma dose beyond these values, chain scission increasingly became the dominant mechanism, as can be observed in the sharp decrease of the molecular weight. Thus, low gamma ray dose of no more than approximately 50 kGy provided the most benefit for increasing the molecular weight of PETE fibers.

3.2. Tensile Strength

PETE fibers with size 1.3 D were irradiated with different gamma ray doses and the tensile strength was evaluated following the ASTM D-2229 standard [21]. Figure 4 demonstrates the results of this test.

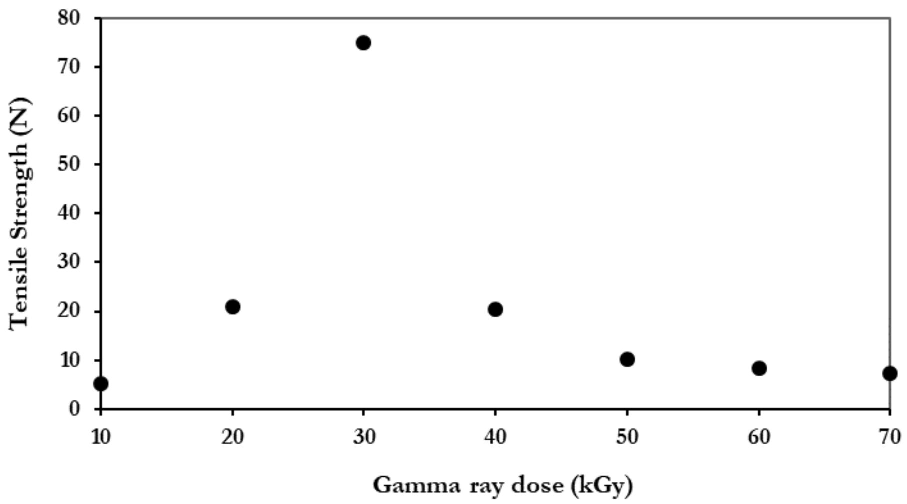


Fig. 4. Results of tensile test following ASTM D-2229 of fiber size 1.3 D treated with different gamma ray doses.

Data in Fig. 4 clearly indicate that the dose of 30 kGy resulted in the highest tensile strength of PETE fibers of approximately 75 N, which is consistent with the molecular weight result in Fig. 3 in that the highest molecular weight provides in the highest tensile strength of the fibers. Also, from 0 – 30 kGy, increasing the radiation dose increased the number of crosslinked polymer chains allowing the fibers to bear more load giving a higher tensile strength. This is an expected behavior of a polymeric material.

3.3. Degree of Crystallinity

PETE fibers with size 1.3 D irradiated with different gamma ray doses were evaluated for the degree of crystallinity using Grande do Sul, Porto Alegre RS, Brazil system. The results are depicted in Fig. 5.

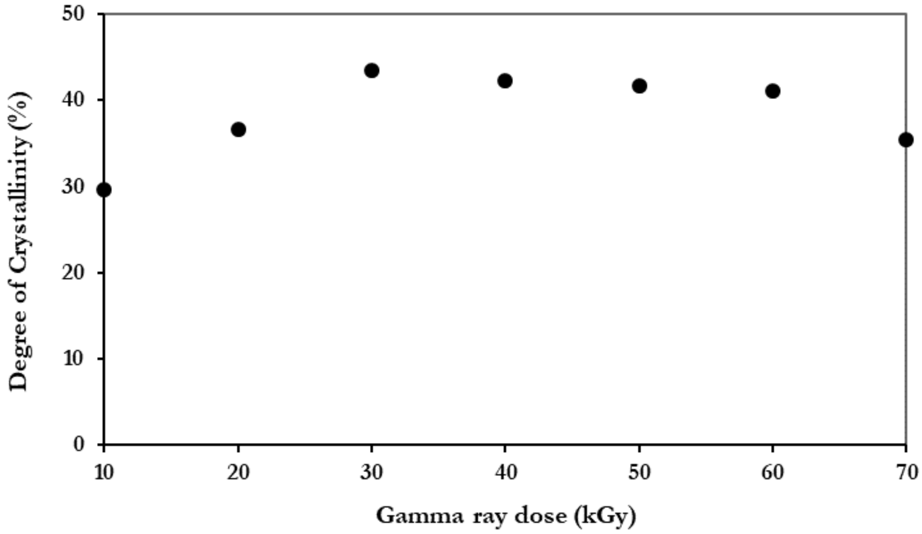


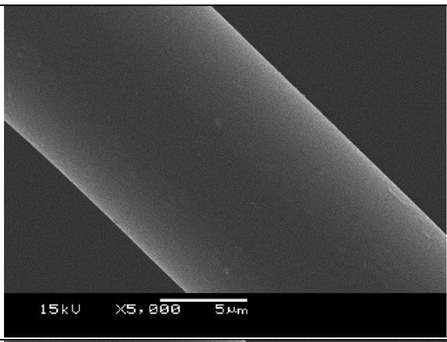
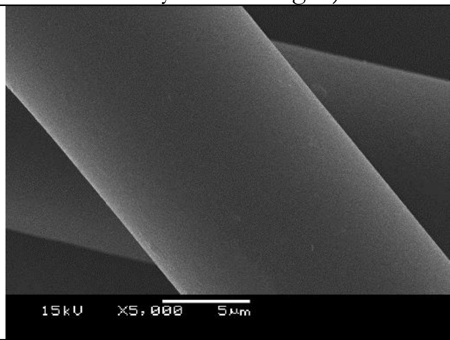
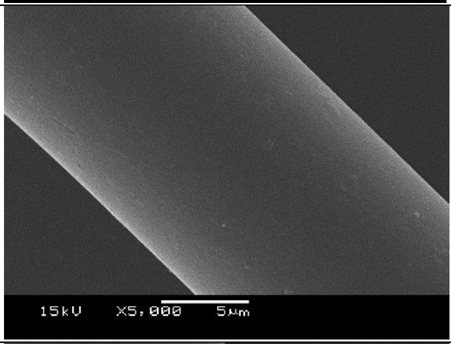
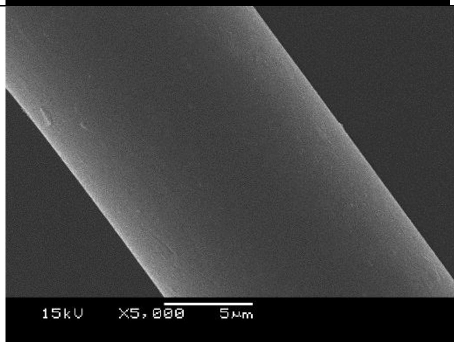
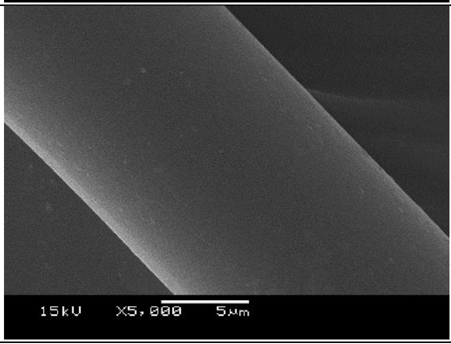
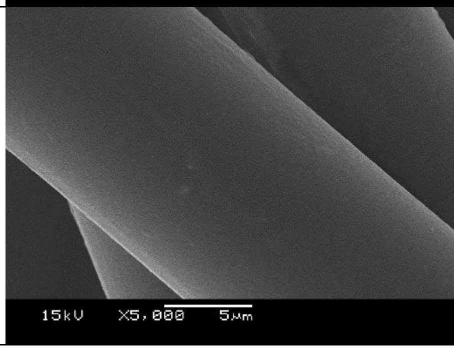
Fig. 5. Results of degree of crystallinity of fiber size 1.3 D treated with different gamma ray doses.

Results in Fig. 5 indicate that the degree of crystallinity of the fibers increased with increasing gamma radiation dose up to 30 kGy, reaching the maximum value of 43.50% at 30 kGy. At higher doses, the degree of crystallinity decreased slightly. The trend of this test is consistent with the trends in the molecular weight test and the tensile test. This behavior can be explained that the increasing degree of crystallinity was due to the removal of the amorphous parts of the PETE fibers during irradiation, since the amorphous part is more reactive to gamma radiation compared to the crystalline part because the cohesive energy density in the crystalline form is much higher than that for the amorphous part. Furthermore, increasing the gamma ray dose beyond 30 kGy could increase free radical formation to the point that these generated radicals eventually degraded the chemical bonds of the crystalline molecules in PETE fibers, resulting in the reduced degree of crystallinity as well as the decreased tensile strength.

3.4. SEM Analysis

SEM micrographs using JSM 5800 LV / JEOL Ltd., Japan (5,000x, 15 kV) shown in Table 3 reveal that the surface morphology of irradiated PETE fibers is not affected by gamma irradiation, irrespective of the size of the fibers. This indicates that gamma ray affects the structure of the fibers at the chemical bonding level rather than at the surface morphology.

Table 3. SEM micrographs of unirradiated and irradiated PETE fibers.

Fiber size	Unirradiated fibers	Irradiated fibers (with optimum gamma ray dose in Fig. 3)
1.3 D		
7 D		
25 D		

3.5. Accelerated Age Testing

For each fiber size, the ones with highest molecular weights were chosen to undergo the accelerated age testing under the strong basic solution. Figure 6 shows the results of the test. The experiment was performed in triplicate and the reported values represent the averaged ones with the corresponding error bars. According to the results, PETE fibers of size 1.3 D, the smallest size used in the experiment, retained the highest molecular weight. Even for up to 60 months of accelerated age testing, the molecular weight was still the highest, indicating that these radiation-treated fibers will maintain their mechanical strength for up to at least 60 months. On the other hand, all fiber sizes without gamma irradiation suffered severe molecular weight reduction.

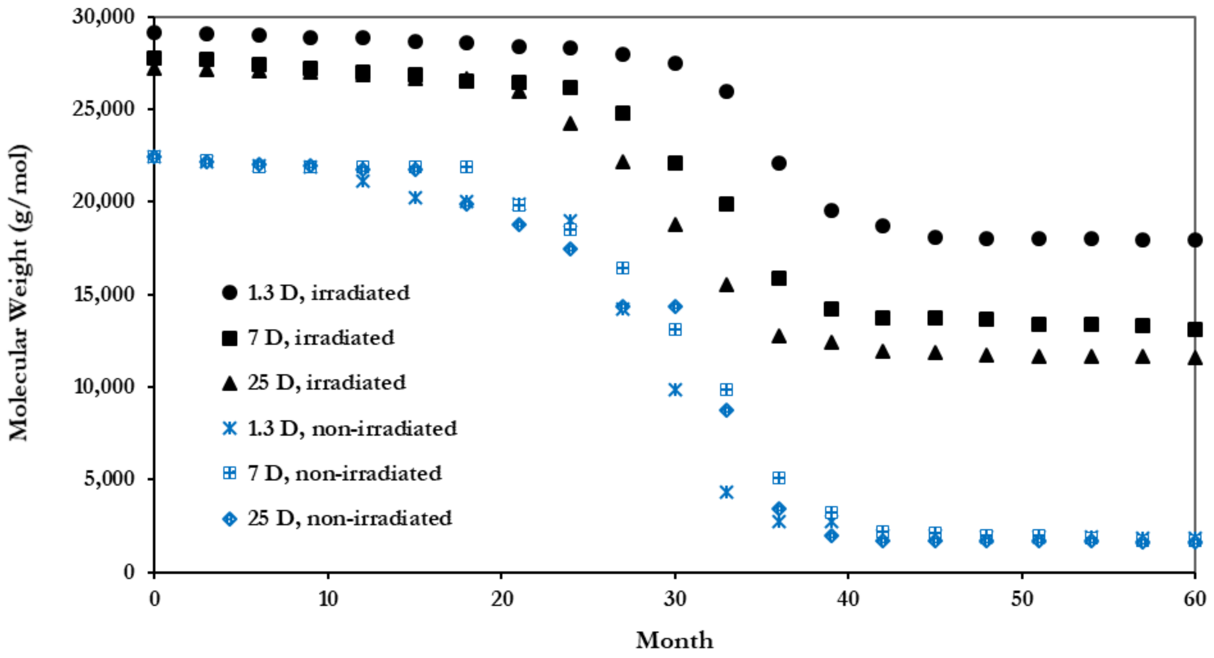


Fig. 6. Effect of strong basic solution on molecular weight reduction of PETE fibers under accelerated age testing.

3.6. Thermal Neutron Attenuation Test

Figure 7 displays the operating voltage vs. neutron count rate in order to determine the optimum operating voltage, which can be calculated to be 844 V.

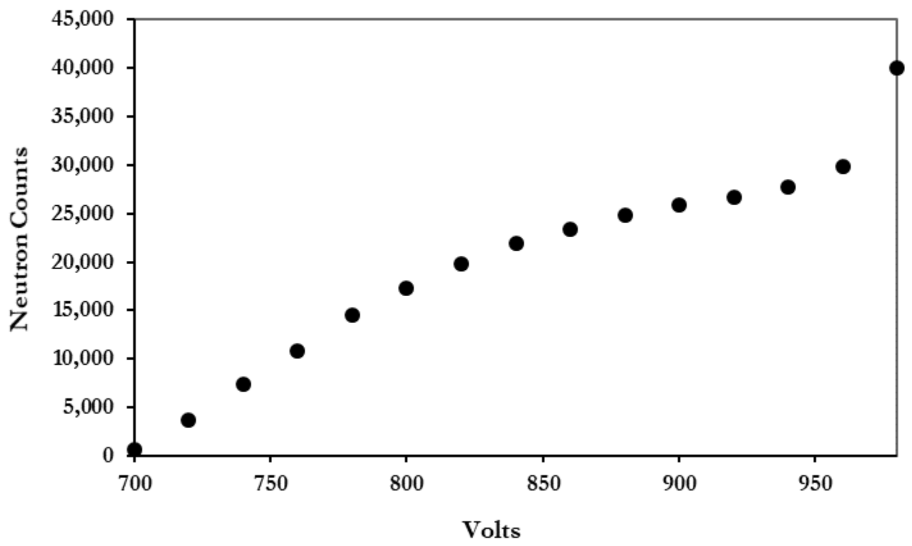


Fig. 7. Operating voltage vs. neutron count rate for determination of optimum operating voltage.

Tables 4 and 5 show the results of the neutron counting measurement for the concrete reinforced with fibers sizes 1.3 D and 25 D. For the case of concrete reinforced with fiber size 1.3 D, the background neutron count was 22 counts/10 minutes and the neutron count without shielding was 3,416 counts/10 minutes. For the case of concrete reinforced with fiber size 25 D, the background neutron count was 18 counts/10 minutes and the neutron count without shielding was 3,412 counts/10 minutes.

Table 4. Results of thermal neutron attenuation of concrete reinforced with PETE fibers with size 1.3 D.

Experiment Number	Neutron counting			
	Without reinforcement	0.1% fiber content	0.2% fiber content	0.3% fiber content
1	2151	1924	1723	1482
2	2247	1966	1766	1501
3	2108	1875	1700	1498
4	2442	1935	1717	1480
5	2095	1893	1663	1483
6	2186	1874	1699	1525
Average	2204	1911	1711	1494
Attenuation compared to unreinforced concrete (%)	---	44.05	49.90	56.24

Table 5. Results of thermal neutron attenuation of concrete reinforced with PETE fibers with size 25 D.

Experiment number	Neutron counting		
	0.1% fiber content	0.2% fiber content	0.3% fiber content
1	1916	1750	1432
2	1955	1760	1447
3	1864	1704	1402
4	1899	1715	1436
5	1901	1644	1480
6	1921	1636	1426
Average	1909	1702	1437
Attenuation compared to unreinforced concrete (%)	44.00	50.10	57.90

Figure7 plots the data from Tables 6 and 7 on thermal neutron attenuation percentages compared to unreinforced concrete to allow observation and interpretation of the trends.

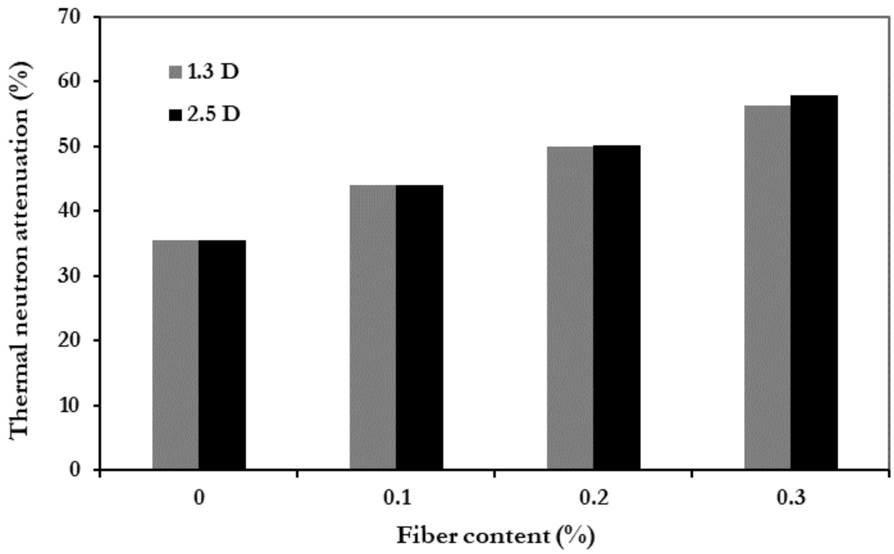


Fig. 7. Evaluated thermal neutron attenuation for both fiber sizes compared to unreinforced concrete.

From Fig. 7, the degree of thermal neutron attenuation increased with increasing PETE fiber content. At 0% fiber content, the concrete alone exhibited neutron reduction of about 35%. When the fiber content reached 0.3%, FRC exhibited the highest thermal neutron attenuation of about 60% compared to unreinforced concrete. These results are expected because PETE fibers are polymeric material composing of H and C atoms. Hydrogen atoms are very effective neutron shield. Thus, by incorporating the material with a much higher hydrogen atom concentration into concrete, the thermal neutron shielding characteristic is expected to be highly enhanced. Moreover, results indicate that the size of fibers did not affect thermal neutron attenuation. This can be implied that the thermal neutron attenuation characteristic depends primarily on the volume fraction of the PETE fibers.

According to all of the presented data, it can be concluded that concrete reinforced with radiation-treated PETE fibers exhibits excellent mechanical stability as well as excellent thermal neutron attenuation compared to unreinforced concrete. These FRCs can readily be utilized as an effective neutron shielding material for nuclear and radiation applications to enhance radiation safety.

4. Conclusion

This study successfully enhanced the stability of PETE fibers in a strong alkali solution typical of concrete using low-dose gamma radiation. The gamma ray dose of only 30 kGy resulted in the highest molecular weight, tensile strength and degree of crystallinity of PETE fibers with size 1.3 D. SEM micrography revealed that the surface morphology of irradiated PETE fibers is not affected by gamma irradiation. The accelerated age testing indicated the acceptable fiber strength inside concrete for up to at least 60 months. On the other hand, fibers without gamma irradiation suffered severe molecular weight reduction in this test. Evaluation of thermal neutron attenuation of FRC showed that the degree of thermal neutron shielding increased with increasing PETE fiber content, and that at 0.3% fiber content, FRC exhibited the highest thermal neutron attenuation of about 60% compared to unreinforced concrete. Therefore, these FRCs can readily be utilized as an effective neutron shielding material for nuclear and radiation applications to enhance radiation safety.

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References

[1] P. Phahontep, *Polymer Science*. Bangkok: Ramkhamheang University Press, 2009, vol. 1.
[2] J. Wootthikanokkhan, "Polymer Characterization and Analysis," Bangkok, 2012.
[3] G. Odian, *Principle of Polymerization*, 4 ed., New York: Wiley-Interscience, 2003.
[4] B. Siriwattana, *Radiation Chemistry and Processing*. Ramkhamheang University Press, 2015.
[5] D. H. Jeon, K. H. Lee, and H. J. Park, "The effects of irradiation on physiochemical characteristics of PET packaging film," *Radiation Physics and Chemistry*, vol. 71, pp. 1059-1064, 2004.
[6] A. Buttafava, G. Consolati, L. Di. Landro, and M. Mariani, "Y-irradiation effects on polyethylene terephthalate studied by positron annihilation lifetime spectroscopy," *Polymer*, vol. 43, no. 26, pp. 7477-7481, 2002.
[7] F. Pacheco-Torgal, Y. Ding, and S. Jalali, "Properties and durablity of concrete containing polymeric wastes (tyre rubber and polyethylene terephthalate bottles)," *Construction and Building Materials*, vol. 30, pp. 714-724, 2012.
[8] V. Kuma, Y. Ali, R. G. Sonkawade, and A.S. Dhaliwal, "Effect of gamma irradiation on the properties of plastic bottle sheet," *Nuclear Instruments and Medthods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 287, pp. 10-14, 2012.
[9] B. Fox, G. Moad, G. van Diepen, I. Willing, and W. D. Cook, "Characterization of poly (ethylene terephthalate) and poly (ethylene terephthalate) blends," *Polymer*, vol. 38, pp. 3035-3043, 1997.

[10] M. Pentimalli, D. Capitani, A. Ferrando, D. Ferri, P. Ragni, and A. L. Segre, "Gamma irradiation of food packaging materials: An NMR Study," *Polymer*, vol. 41, pp. 2871-2881, 2000.

[11] F. Pelissera, O. R. K. Montedo,, P. J. P. Gleize, and H. R. Roman, "Mechanical properties of recycled PET fibers in concrete," *Material Research*, vol. 15, no. 4, pp. 679-686, 2012.

[12] T. Ochi, S. Okubo, and K. Fukui, "Development of recycled PET fiber and its application as concrete-reinforcing fiber," *Cement & Concrete Composites*, vol. 29, pp. 448-455, 2012.

[13] M. Alexander and S. Mindess, "Special aggregates and special concrete," in *Aggregates in Concrete*. CRC Press, 2005, pp. 361-368.

[14] A. Sivakumar and M. Santhanam, „Mechanical properties of high strength concrete reinforce with metallic and non-metallic fibers," *Cement and Concrete Composites*, vol. 29, no. 8, pp. 603-608, 2007.

[15] H. Kong, S. G. Bike, and V. C. Li, "Development of a self consolidating engineered cementitious composite employing electrosteric dispersion/stabilization," Chem. Concr. Compos, vol. 25, no. 3, pp. 301-309, 2003.

[16] G. Odian, *Principle of Polymerization*. New York: John Wiley & Sons, 2004, pp. 93-96.

[17] P. Petiraksakul, *Elements of Polymers 1*, 2 ed. Bangkok: Ramkhamhaeng University Press, 2009, vol. 2, pp. 70-75.

[18] D. H. Jeon, K. H. Lee, and H. J. Park, "The effects of irradiation on physiochemical characteristics of PET packaging film," *Radiation Physics and Chemistry*, vol. 71, no. 5, pp. 1059-1064, 2004.

[19] M. Kattan, "Thermal behavior of gamma-irradiated amorphous poly (ethylene terephthalate) films," *Polymer Engineering and Science*, vol. 46, no. 10, pp. 1374-1377, 2006.

[20] J. C. M. Suarez, E. B. Mano, and C. M. C. Bonelli,, "Effects of gamma-irradiation on mechanical characteristics of recycled polyethylene blend," *Polymer Engneering and Science*, vol. 39, no. 8, pp. 1398-1403, 1999.

[21] *Adhesion between Steel Tire Cords and Rubber*, ASTM Standard D-2229.